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(54) **Toothpaste**

(57) A hazed toothpaste which can effect dental remineralization and reduce caries formation contains a binary fluorine-providing system which provides 750-1225 ppm fluoride from sodium monofluorophosphate and 50-1000 ppm fluorine from sodium fluoride, a synthetic precipitated siliceous polishing agent, and dicalcium phosphate. Additional haze to permit opacification of the toothpaste may be introduced by the presence of an opacifying agent, such as titanium dioxide.

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SPECIFICATION

Toothpaste

The present invention relates to a toothpaste which promotes oral hygiene and which is also stabilized against gassing in an unlined aluminium tube and against colour fading, should a water-soluble dye be present, and which desirably has a hazed appearance.

In the past, toothpastes have been used which contain a single fluorine-providing agent such as sodium fluoride, stannous fluoride or sodium monofluorophosphate (it being understood that a minor part of commercial sodium monofluorophosphate consists of sodium fluoride).

Recently, as in British Patent 1,435,624 of Beecham Group and U.S. Patent 4,152,419 of Colgate-Palmolive toothpastes for promoting oral hygiene have come to prominence which contain two separately added fluorine-providing agents (that is, a binary system) namely sodium fluoride and sodium monofluorophosphate.

In previous practice, synthetic precipitated siliceous material has been described as a desirable polishing agent in toothpastes containing a single fluorine-providing agent, such as sodium monofluorophosphate. Such a polishing agent tends to cause gassing when the fluorine-providing toothpaste is in an unlined aluminium tube. It has been proposed to overcome this by contacting the siliceous material with calcium, either by pretreatment or in situ. This has been described in U.S. Patents 4,141,969 of Colgate-Palmolive and 4,159,280 of J. M. Huber.

It has been observed that in toothpaste containing a binary fluorine-providing system of sodium monofluorophosphate and sodium fluoride whether or not synthetic precipitated siliceous polishing agent is pretreated with calcium, gassing in an unlined aluminium tube occurs and colour fading occurs when a water-soluble dye is present.

It is an object of this invention to provide a toothpaste containing sodium fluoride and sodium monofluorphosphate with a desirable degree of soluble fluorine retention which promotes oral hygiene, for instance, by reducing caries formation and which can effect dental remineralization in which the toothpaste contains dicalcium phosphate which stabilizes it against gassing when packaged in an unlined aluminium toothpaste tube and against colour fading when a water-soluble dye is present and which may also haze the appearance of the toothpaste. Thus, we have found that, the presence of dicalcium phosphate or ions provided therefrom or both stabilizes toothpastes containing sodium fluoride and sodium monofluorophosphate.

According to the present invention a toothpaste comprises a binary fluorine-providing system which provides about 750-1225 ppm fluorine from sodium monofluorophosphate and about 50-1000 ppm fluorine from sodium fluoride and about 15-40% by weight of a synthetic precipitated siliceous polishing agent wherein there is present about 0.1-2.5% by weight of dicalcium phosphate or ions thereof which stabilizes it against gassing when packaged in an unlined aluminium toothpaste tube and against colour fading when the toothpaste contains a water-soluble non-toxic dyestuff.

Sodium monofluorophosphate is employed in an amount to provide about 750-1225 ppm fluorine to the toothpaste. This corresponds to about 0.5-1% by weight of sodium monofluorophosphate in the toothpaste. The preferred amount is about 0.76-0.874% which provides about 1000-1150 ppm fluorine to the toothpaste.

Sodium monofluorophosphate, Na_2PO_3F, as commercially available may vary considerably in purity. It may be used in any suitable purity provided that any impurities do not substantially adversely affect the desired properties. In general, the purity is desirably at least 80%. For best results, it should be at least 85%, and preferably at least 90% by weight of sodium monofluorophosphate with the balance being primarily impurities or by-products of manufacture such as sodium fluoride and water-soluble sodium phosphate salt. Expressed in another way, the sodium monofluorophosphate employed should have a total fluoride content of above 12%, preferably above 12.7%, a content of not more than 1.5%, preferably not more than 1.2% of free sodium fluoride; and a sodium monofluorophosphate content of at least 12%, preferably at least 12.1% all calculated as fluorine.

Sodium fluoride is separately added to provide an additional fluorine amount of about 50-1000 ppm (for example 50-500 ppm). This corresponds to about 0.01-0.1% of sodium fluoride. Thus, 50-100 ppm, corresponds to about 0.01-0.02% of sodium fluoride.

The polishing agent is a synthetic precipitated siliceous material which may be essentially silica. Preferably it contains up to about 1% by weight of alumina interbonded therein. Such polishing materials may also be considered to be aluminosilicates, particularly sodium aluminosilicates. Typical examples are described in U.S. Patent 3,906,090 of Colgate-Palmolive and in U.S. Patents 4,015,996, 4,105,757, and 4,122,160 of J. M. Huber. Examples of these materials are ZEO 49 and ZEO 49B of Huber and Tixosil 53 of Sifrance. The polishing agent is employed in amounts of about 15-40% by weight, preferably about 15-30% e.g. 15-20% or about 25-30%.

The toothpaste containing the synthetic precipitated siliceous polishing agent typically has the consistency of a gel. Since the polishing agent may have a refractive index close to that of the liquid vehicle of the toothpaste (e.g. glycerol or sorbitol or mixtures thereof and a minor amount of water), the toothpaste is typically essentially clear to translucent in the absence of a hazing or opacifying agent. In accordance with the present invention the toothpaste gel is desirably made more hazy, that is made less clear and more translucent with the inclusion of about 0.1-2.5% by weight of a hazing agent. Dicalcium phosphate, including dicalcium phosphate dihydrate and anhydrous dicalcium phosphate and mixtures thereof has a hazing function and may be the hazing agent employed. Dicalcium phosphate modifies the polishing characteristics of the toothpaste. It also has a particularly marked effect, even in the minor hazing amount employed, in stabilizing the toothpaste against gassing when it is packaged in an unlined aluminium tube and in stabilizing the toothpaste

against dye fading when a water soluble dyestuff is present. It is preferably present in an amount of about 0.1-1% by weight, most preferably about 0.5-1%, typically about 0.5% or 0.1 to 0.5%.

In addition to dicalcium phosphate, the degree of haze of the toothpaste may be increased by the presence of a small amount of an additional agent, typically in amount of less than 0.05% preferably less than 0.02% by weight, e.g. 0.01 to 0.015%. Typical agents include titanium dioxide and substantial equivalents thereof, such as zinc oxide. Titanium dioxide is preferred for inclusion in toothpaste. Such agents are often considered to be opacifying agents. However, the amounts set forth herein are not sufficient to opacify the toothpaste but rather abet hazing.

The liquid vehicle of the toothpaste preferably contains about 20-80% by weight of humectant such as glycerol, sorbitol, or polyethylene glycol e.g. polyethylene glycol 600 or mixtures of humectants. A toothpaste typically contains about 20-30% by weight of glycerol and about 30-60% by weight of sorbitol (e.g. as a 70% solution) i.e. 21% to 42% e.g. 20-45% actual sorbitol.

Water (free of association with other components such as sorbitol) may be present too in amounts of up to about 50% by weight, typically about 1-10% in a low water composition or about 15-40% in a higher water formulation. In the absence of hazing agents, the low water toothpaste typically would be more translucent or transparent in appearance than the higher water toothpaste.

Further, in the absence of the dicalcium phosphate hazing agent the toothpaste containing the binary fluoride system and siliceous polishing agent is prone to form gas in the presence of and be incompatible with an unlined aluminium tube. This is particularly marked when the water content is high, e.g. above about 25% by weight. However, it is observable even in a low water toothpaste.

When a water-soluble non-toxic dyestuff which is susceptible to colour fading is present, e.g. in amount of about 0.001-0.1% by weight, colour fading in the absence of dicalcium phosphate hazing agent visibly occurs in both the higher water and lower water toothpaste.

The toothpaste also typically includes a gelling agent such as a natural or synthetic gum or gumlike material e.g. Irish moss, gum tragacanth, sodium carboxymethylcellulose, polyvinylpyrrolidone, xanthan, guar gum or starch or mixtures thereof.

Sodium carboxymethyl cellulose is preferred. The gelling agent content is typically present in an amount of about 0.1-5% by weight preferably about 0.1-0.5%. The gelling effect can be supplemented with about 5-10% by weight preferably about 6.5-8%, e.g. about 7-8% of a filler such as a pyrogenic silica or a silica aerogel. Zeosyl 200 of J. M. Huber is a desirable silica filler material. "Zeosyl" is a trademark.

Any suitable surface active or detersive material may be included in the toothpaste. Such compatible materials are desirable to provide additional detersive, foaming and antibacterial properties depending upon the specific type of surface active material and are selected appropriately. These detergents are water-soluble compounds usually, and may be anionic, nonionic or cationic in structure. It is usually preferred to use the water-soluble non-soap or synthetic organic detergents. Suitable detersive materials are known and include, for example, the water-soluble salts of higher fatty acid monoglyceride monosulphate detergents (e.g. sodium coconut fatty acid monoglyceride monosulphate), higher alkyl sulphates (e.g. sodium lauryl sulphate), alkyl aryl sulphonates (e.g. sodium dodecyl benzene sulphonate), and higher fatty acid esters of 1,2 - dihydroxy propane sulphonate.

Further surface active agents include the substantially saturated higher aliphatic acyl amides of lower aliphatic amino carboxylic acid compounds, such as those having 12 to 15 carbons in the acyl radical. The amino acid portion is derived generally from the lower aliphatic saturated monoaminocarboxylic acids having about 2 to 6 carbons, usually the monocarboxylic acid compounds. Suitable compounds are the fatty acid amides of glycine, sarcosine, alanine, 3 - aminopropanoic acid and valine having about 12 to 16 carbons in the acyl group. It is preferred to use the N - lauroyl, myristoyl and palmitoyl sarcoside compounds, however for optimum effects.

The amide compounds may be employed in the form of the free acid or preferably as the water soluble salts thereof, such as the alkali metal, ammonium, amine or alkylolamine salts. Specific examples thereof are sodium and potassium N - lauroyl, myristoyl and palmitoyl sarcosides, ammonium and ethanolamine N - lauroyl sarcoside, N - lauroyl sarcosine, and sodium N - lauroyl glycide and alanine.

The surface active agent is typically employed in an amount of about 1-5% by weight, preferably about 1-3%, this latter amount being preferred for sodium lauryl sulphate.

Any suitable flavouring or sweetening materials may be employed in formulating a flavour for the toothpaste of the present invention. Examples of suitable flavouring constituents include the flavouring oils, e.g. oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, marjoram, cinnamon, lemon and orange, as well as methylsalicylate. Suitable sweetening agents include sucrose, lactose, maltose, sorbitol, sodium cyclamate and sodium saccharine. Sodium saccharine is preferred. Flavour is typically present in an amount of about 0.5-1.5% by weight, preferably about 1% and sweetener in an amount of about 0.1-0.2%.

If desired visible particles of pearlescent flakes, such as titanium dioxide coated mica flakes, may be distributed in the toothpaste, typically in amount of about 0.1-0.3% by weight. Likewise, the toothpaste may be striped.

The toothpaste should have a pH practicable for use. A pH range of about 5 to 10 is particularly desirable. The pH may be adjusted as desired with appropriate acidic or alkaline materials such as citric acid sodium hydroxide. The reference to the pH refers to the pH determined directly on the toothpaste. Stabilizers such as sodium benzoate may be used.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to

the accompanying Examples.

All amounts are by weight unless otherwise specified.

EXAMPLES 1A and 1B

Example 1A is a comparison example.

The following toothpastes were prepared and placed in unlined aluminium tubes:

Examples	A	B
INGREDIENTS	PARTS	
Glycerine	25.00	25.00
Sodium carboxymethyl cellulose	1.00	1.00
Sodium saccharin	0.30	0.30
Titanium dioxide	0.01	0.01
FD & C Blue No. 1 (1% solution)	0.20	0.20
Polyethylene Glycol 600	3.00	3.00
Synthetic precipitated silica (ZEO 49 - contains about 50 ppm of calcium)	28.00	28.00
Dicalcium phosphate dihydrate	-	0.50
Sodium monofluorophosphate	0.76	0.76
Sodium fluoride	0.10	0.10
Sodium lauryl sulphate	1.76	1.76
Flavour	0.65	0.65
Deionized water	Q.S. to 100	Q.S. to 100

Each of the toothpastes of Examples 1A and 1B was translucent, toothpaste 1B being hazier than toothpaste 1A due to the presence of the dicalcium phosphate dihydrate. Upon aging for 1 month at 43°C, at 4°C and at room temperature, gas formation occurred in the tubes containing the toothpaste of Example 1A and the initial colour due to the dye faded. In the tubes at 43°C and at room temperature the inner surfaces of the tubes were attacked, with actual explosion of the tube occurring with the one aged at 43°C. In the case of the toothpaste of Example 1B, no gassing, tube attack or dye fading were observed upon aging for 1 month at 43°C, at 4°C and room temperature.

EXAMPLES 2A, 3A and 2B and 3B

Examples 2A and 3A are comparison examples.

The following translucent toothpaste was prepared and placed in unlined aluminium tubes:

INGREDIENTS	PARTS
Glycerine	25.00
Sodium carboxymethyl cellulose	0.26
Sodium saccharin	0.20
Titanium dioxide	0.015
FD & C Blue No. 1 (1% solution)	0.19
Synthetic precipitated silica (Tixosil 53 - contains about 600 ppm of calcium)	17.00
Silica filler (Zeosyl 200)	7.00
Sodium monofluorophosphate	0.76
Sodium fluoride	0.10
Sodium lauryl sulphate	1.76
Flavour	1.00
Deionized water	3.00
Sorbitol (70%)	Q.S. to 100

This toothpaste upon aging for 3 months at 43°C, at 4°C and room temperature resulted in gas formation in the tube. Further the initial dye colour faded. Substantial instability was also observed after 1 month.

EXAMPLE 3A

Similar instability occurred when Tixosil 53 was replaced by Zeo 49.

EXAMPLES 2B and 3B

When 0.10 part of dicalcium phosphate dihydrate was incorporated into the toothpastes of Examples 2A and 3A which contain Zeo 49 and Tixosil 53 respectively, the products became hazier and upon aging remained stable in the tubes while retaining intensity of dye colouring.

CLAIMS

1. A toothpaste comprising an oral vehicle, a binary fluorine-providing system which provides about 750-1225 ppm fluorine from sodium monofluorophosphate and about 50-1000 ppm fluorine from sodium fluoride and about 15-40% by weight of a synthetic precipitated siliceous polishing agent wherein there is present about 0.1-2.5% by weight of dicalcium phosphate which stabilizes it against gassing when packaged in an unlined aluminium toothpaste tube and against colour fading when the toothpaste contains a water-soluble non-toxic dyestuff.

2. A toothpaste comprising an oral vehicle, a binary fluorine-providing system which provides about 750-1225 ppm fluorine from sodium monofluorophosphate and about 50-1000 ppm fluorine from sodium fluoride and about 15-40% by weight of a synthetic precipitated siliceous polishing agent wherein there is present about 0.1-2.5% by weight of dicalcium phosphate which is free of titanium dioxide or contains less than 0.05% thereof.

3. A toothpaste comprising an oral vehicle, a binary fluorine-providing system which provides about 750-1225 ppm fluorine from sodium monofluorophosphate and about 50-1000 ppm fluorine from sodium fluoride and about 15-40% by weight of a synthetic precipitated siliceous polishing agent wherein there is present about 0.1-2.5% by weight of dicalcium phosphate which contains a water-soluble non-toxic dyestuff susceptible to colour fading in the said toothpaste in the absence of the said dicalcium phosphate.

4. A toothpaste as claimed in Claim 3 containing 0.001 to 0.1% of the said dyestuff.

5. A toothpaste as claimed in any one of Claims 1 to 4 which has a hazed appearance.

6. A toothpaste as claimed in any one of Claims 1 to 5 in which sodium monofluorophosphate provides about 1000-1150 ppm fluorine.

7. A hazed toothpaste as claimed in any one of Claims 1 to 6 in which sodium fluoride provides about 50-500 ppm fluorine.

8. A toothpaste as claimed in any one of Claims 1 to 7 in which the said siliceous polishing agent contains up to about 1% by weight of alumina interbonded therein.

9. A toothpaste as claimed in any one of Claims 1 to 8 in which the said siliceous polishing material is present in amount of about 15-20% by weight.

10. A toothpaste as claimed in any one of Claims 1 to 9 in which the siliceous polishing material is present in an amount of about 25-30% by weight.

11. A toothpaste as claimed in any one of Claims 1 to 10 in which the said dicalcium phosphate is dicalcium phosphate dihydrate.

12. A toothpaste as claimed in any one of Claims 1 to 11 in which the said dicalcium phosphate is present

in amount of about 0.1-1% by weight.

13. A toothpaste as claimed in any one of Claims 1 to 12 in which a non-toxic water-soluble dye is present in amount of about 0.1-1% by weight.

14. A toothpaste as claimed in Claim 1 substantially as specifically described herein with reference to any one of the accompanying examples 1B, 2B or 3B.

15. A toothpaste as claimed in any one of Claims 1 to 14 when packaged in an unlined aluminium toothpaste tube.

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